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EVALUATION OF SOLID LUBRICANTS: THE CHEMISTRY OF SPUTTERED MoS$_X$ FILMS USING COMBINED THIN FILM ANALYSIS TECHNIQUES

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ABSTRACT

Thermal desorption spectroscopy (TDS) is introduced as a diagnostic tool for determining the thermal stability of solid lubricant films. In particular, TDS revealed the temperatures at which various decomposition processes occurred as sputtered films were heated in vacuum. The primary film decomposition products detected were SO_2 beginning at about 425K and S_2 beginning at about 1150K. A close relationship between water desorption beginning about 400K and SO_2 desorption exists in the temperature range 400K-800K. Besides chemical decomposition products, a significant amount of argon trapped in the film during the sputtering process is released at various temperatures. TDS results for sputtered films were compared with results for burnished films and with thermo-gravimetric (TGA) analysis, water absorption, and other relevant studies of molybdenum disulfide found in the literature. TDS also showed the N^+ ion-beam modification of sputtered films resulted in a decrease in desorption of SO_2. Along with TDS, X-ray photoelectron spectroscopy (XPS) was used to study the effect of heating on the solid lubricant films. In addition, scanning electron microscopy (SEM), wavelength dispersive spectroscopy (WDS), and Rutherford backscattering spectroscopy (RBS) were used to characterize the samples.

INTRODUCTION

Molybdenum disulfide (MoS_2), tungsten disulfide (WS_2) and other similar transition metal dichalcogenides (eg. sulfides and selenides) have a layered crystal structure with strong bonding in each layer and weaker bonding between layers. The weaker bonding results in a low resistance to shearing during sliding which produces low friction.[1,2] Molybdenum disulfide is commonly used as a lubricant in vacuum environments and in many aerospace applications. In other environments however, such as in the presence of moisture or oxygen, chemical reactions may limit the lifetime of the lubricant.[2-6]

When two materials are in sliding contact, frictional forces induce localized heating, and in the near surface region high temperatures can be reached, even in well lubricated systems.[7,8] At increased temperatures the solid lubricant film can undergo chemical reaction with environmental gases, with gases adsorbed on or in the film, with impurities, and with contaminants introduced during application. These chemical reactions may degrade the film's lubricating ability and lead eventually to lubricant failure. Vapor pressure studies of bulk molybdenum disulfide and tungsten disulfide powders in vacuum, have shown that at higher temperatures (>1200K), dissociation takes place with the liberation of sulfur vapor.[9,10] Therefore, at some temperature dissociation also plays a role in the degradation of the film.

Various analytical techniques can contribute to an understanding of the degradation of lubricant films and thereby improve the understanding of their tribological behavior. Surface analytical techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been used to determine the elemental composition and chemical states for tribological systems. Examples of these studies applied to molybdenum disulfide are, the

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effects of air and moisture on burnished[11] and radio frequency (rf) sputtered films,[3,12] the effects of chemical vapors on a single crystal,[13-15] burnished film-substrate adhesion,[16,17] and the thermal annealing behavior of oxygen-containing rf-sputtered films.[18]

Another analytical technique called thermal desorption spectroscopy (TDS), is useful in the study of degradation processes and involves monitoring the species vaporizing from a surface or a film while the temperature is raised, usually in a linear fashion. Since the TDS technique is sensitive to sub-monolayer quantities of material, it can provide detailed information on a solid film.[19] From the results presented here, TDS is shown to be useful in simulating thermal decomposition occurring in an actual tribological environment. With this technique the degrading effects of adsorbed gases, impurities, and contaminants on lubricant films can be better understood. Furthermore, effects of additives, binders, stabilizers, and co-lubricants on film thermal stability could be determined.

In the present investigation, the TDS techniques previously developed to identify degradation products and the temperatures at which they appear for burnished MoS_2 films,[20] are applied to sputtered MoS_x, burnished MoS_2, and ion-implanted MoS_x and MoS_2 films. In addition, XPS, AES, and wavelength dispersive spectroscopy (WDS) were used to characterize the films before and after heating in a TDS experiment. Finally, scanning electron microscopy (SEM) and Rutherford backscattering spectroscopy (RBS) complimented the other techniques and the combined results provided additional insight into film composition and processes effecting film thermal stability.

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EXPERIMENTAL

A. TDS Evaluation System

The main evaluation system, referred to as the "TDS-system", was pumped with a mercury diffusion pump fitted with a liquid nitrogen trap and could obtain pressures in the low 10^{-10} torr range. Experiments on solid lubricant films, however, were performed after baking the system to about 325K which gave pressures in the low 10^{-9} torr range. The sample holder conveniently held three samples but could hold several more. A schematic diagram of the system is shown in Fig.1. Each sample was positioned and heated individually so that the gaseous species evaporating from the surface entered a specially modified mass spectrometer ionizer by a line of sight path of approximately 6 cm. The mass spectrometer contained a quadrupole filter, a copper-beryllium dynode electron multiplier, and an electron impact ionizer with an electron energy set to 70 eV. The spectrometer mass scale was calibrated using perfluorotributylamine. In addition, the evaluation system contains Auger-LEED equipment as well as facilities for laser heating of samples. Unless noted otherwise, thermal desorption was done using the TDS-system.

B. Sample Preparation

Sputtered and burnished solid lubricant films were supported on 0.05 mm thick tantalum foil which was first cleaned chemically and then heated to about 1200K in vacuum. The chemical cleaning procedure involved sonicating foils in trichloroethylene, then in ethanol, and then drying in air. Following this, the foils were soaked in aqua regia (3 parts conc. HCl to 1 part conc. HNO_3) and then rinsed several times in deionized water and finally dried under a heat lamp. A clean tantalum foil 25mm x 75mm was screwed down at it's edges to a stainless steel plate and then two other identical foils were fastened in such a way as to mask all but a strip 5mm x

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75mm running down the center of the first foil. In the coating process only this unmasked area of the first foil is coated. After coating, the foils were removed from the plate and could be cut to fit various applications (e.g. TDS, SEM, etc.). The lubricant coating was applied by DC triode sputtering of an MoS_2 target in an argon plasma[21] or by burnishing MoS_2 crystals (99% pure) with a cotton applicator using a force of 5 grams. No efforts were made to control the burnishing environment.

For studies in the TDS-system, after removal from the plate, the foil with the strip of lubricant coating was cut into 5mm x 25mm samples running perpendicular to the coated strip producing about 13 separate samples. Each of these had a coated area of 5mm x 5mm in the center. In Fig.2 the sample assembly is shown which provided sample heating and temperature measurement. The length of the sample holder is about 55mm. As seen in Fig.2-2, the uncoated portion of the 5mm x 25mm foil is bent over and the foil is attached to the holder so the coated portion (Fig.2-1) is at the top facing the mass spectrometer.

C. Temperature Control

Temperature was measured with a calibrated (3 percent Re/W)-(25 percent Re/W) thermocouple pair spotwelded to the back of each sample. Several of these sample holders were then attached to the multiple sample holder shown in Fig.1. Each sample was studied in turn by positioning in front of the mass spectrometer followed by programmed heating to temperatures up to 2000K. The thermocouple signal was compared to a reference voltage and the difference was used to control the output of the heater power supply. The reference voltage was programmable and was adjusted to give a ramp rate of 7.5 K/sec. The thermal desorption technique has been developed over several decades and a large number of references exist. It

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should therefore suffice to direct the reader to a few selected references for further description of the technique.[22-24]

D. XPS-TDS Evaluation System

A second analysis system which consisted of two chambers is shown in Fig.3. This system was turbopumped, liquid nitrogen-trapped and is be referred to as the "XPS-TDS system". It was used for the combined XPS and TDS studies TDS was performed in the first chamber which was fitted with a sputter ion gun for cleaning and a mass spectrometer. A second chamber containing Auger and XPS equipment was used for elemental and chemical analysis. A heated sample probe allowed the sample to be transferred from atmosphere into the TDS chamber, then into the XPS chamber. Figure 4 shows an expanded view of the sample area within the heated probe. The solid lubricant coated tantalum foil sample shown in Fig.4-4, is tightly fastened to the probe heater block with screws and washers to ensure good thermal contact. The probe temperature could be ramped at different rates to a maximum of 1050K. Samples were first studied with XPS, then with TDS and finally reexamined with XPS. X-ray photoelectron spectra were taken in both survey (0-1keV) and high resolution modes. The XPS-TDS system includes a hemispherical electron energy analyzer, Mg and Al X-ray anodes, as well as an electron gun for Auger studies. The electron energy analyzer was calibrated using a gold standard that was cleaned by argon ion sputtering.

E. Mass Spectrometer Control

A microcomputer-based mass spectrometer data system controlled the quadrupole mass filter, recorded ion currents and temperature, and initiated the heating of the sample. Survey experiments were performed first in which the mass spectra were continually recorded as the

sample temperature was ramped. The high limit of the mass range in the TDS-system was 340 amu and 1200 amu for the XPS-TDS system. Next, the experiment was repeated but only those masses indicated by the survey were monitored as shown in Table 1. This increased the signal to noise ratio and high resolution TDS spectra were obtained. The vapors produced by molybdenum oxides when heated are known to contain significant quantities of high molecular weight species. The species which are known to vaporize from pure molybdenum trioxide are primarily $(MoO_3)_x(g)$ (x=3,4,5) with smaller amounts of monomer and dimer.[25] For molybdenum dioxide the vaporizing species are $(MoO_3)_x(g)$ (x=1,2,3) and $MoO_2(g)$.[26]

F. Other Analysis Methods

TDS and XPS analysis were performed on sputtered MoS_x and burnished MoS_2 films which were ion-implanted. The procedure involved fastening coated foils onto a heat sinked copper platen and implanting the surface with a non-mass selected ion beam containing N^+(10 percent N_2^+) impinging normal to the film surface.[20] The dose and energies used were $2 \times 10^{17}/cm^2$ at 60keV for the sputter coated film and $3 \times 10^{17}/cm^2$ at 86 keV for the burnished film.

The sputtered film thickness was determined by scraping away the film with a razor blade which produced a well defined terminal edge of the coating. The height of this edge was determined within about 10% using scanning electron microscopy with the electron beam incident at an angle 70 degrees from the surface normal and a 10,000x magnification. SEM was also used to observe changes in the morphology of films as a result of heating and N^+ ion-implantation. Along with SEM, wavelength dispersive spectroscopy (WDS) using a pentaerythritol (PET) crystal, was used to determine the change in the S:Mo ratio as a result of heating. Absolute standards were not used in the calibration procedure so only relative changes in film composition

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as a result of heating were determined.

To determine the stoichiometry of the sputtered film, Rutherford backscattering spectroscopy (RBS) analysis was performed with a 2 MeV He^{++} beam. The energy scale was calibrated using gold, titanium, oxygen and carbon. In an attempt to minimize interference from a strong tantalum substrate signal, the ion beam was set at a 65 degree angle from the surface normal. This allowed a determination of the S:Mo ratio in the film, however elements lighter than sulfur (e.g oxygen) were obscured by the tantalum substrate signal.

RESULTS

In the TDS experiments, a survey was done first, and desorption spectra were obtained over a wide mass range. Typically the masses monitored ranged from a low of 12 amu for the atomic carbon ion $[C^+]$ to a high of 290 amu for $[(MoO_3)_2^+]$ and in some cases as high as 435 amu for $[(MoO_3)_3^+]$. Many decomposition products were detected, but only a few were predominant. Next, to obtain high resolution spectra, the experiment was performed again on another member of the sample set. Here, only the masses indicated by the survey were monitored. Table 1 gives a list of the masses and relative peak areas (average of 4 samples) for sputtered MoS_x coatings.

Figure 5 shows the 40 amu (Argon) and the 64 amu (S_2 and SO_2) desorption spectra of a sputtered film. Since sulfur has major isotopes of 32 and 34 amu, a comparison of the areas of the 64 amu (M) and the 66 amu (M+2) peaks can be used to distinguish between S_2 and SO_2. If the molecule has one sulfur atom, as in SO, SO_2, and SO_3, the ratio of the areas for the (M) and the (M+2) ion peaks should give $[(M+2)/M]=4.44\times10^{-2}$, but when two sulfur atoms are

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present a ratio of 8.89x10^{-2}, as in S$_2$, CS$_2$ and S$_2$O.[27] Besides the isotope ratio, the two can be distinguished since SO$_2$ will produce a 48 amu desorption spectrum along with the 64 amu. This is a result of the SO$^+$ fragment produced by electron impact ionization of SO$_2$ in the mass spectrometer. The low temperature 64 amu peaks with maxima at 627K and 752K and the shoulder at 486K were all identified as SO$_2$. The larger 64 amu peak with a maximum at 1402K gave [(M+2)/M]=7.21x10^{-2} indicating S$_2$ and some SO$_2$. The first decomposition product detected from a sputtered film was SO$_2$, beginning at about 425K. The SO$_2$ and S$_2$ shown in Fig.5 are the predominant decomposition products observed with TDS. In one experiment the heating was stopped immediately after the high temperature peak finished, at about 1500K. Using WDS it was possible to determine the amount of molybdenum and sulfur before and after heating. It was found that the film released 96 percent of the total sulfur when heated to this temperature. This was interpreted to mean that the 64 amu spectrum (SO$_2$ and S$_2$) in Fig.5, represents most of the sulfur in the film.

In Fig.5, the argon desorption spectrum at 40 amu is shown along with the 64 amu spectrum. The presence of argon is not surprising since the films were produced in an argon plasma. Since argon does not form strong bonds, it must be trapped in the film. In Fig.5, the area of the 40 amu (argon) peaks are roughly comparable to the 64 amu (SO$_2$ and S$_2$) peaks, but because the instrument's sensitivity varies with the ionization characteristics and the mass of the species being detected, no quantitative comparison can be made without a calibration. There are several releases of argon and the first appears to be related to the lower temperature SO$_2$ states, while the final one is clearly related to the S$_2$ and SO$_2$ at higher temperature. No previous report of argon in this type of film has been found in the literature. Any effects of the argon

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incorporation on the film lubrication properties or film stability is unknown at this time.

Both XPS and Auger survey spectra of a sputtered film showed that the chemical composition at the surface was sulfur, molybdenum, oxygen, and a small amount carbon. Previous reports suggest the presence of an oxide layer[3,12], and recently the presence of oxygen in the bulk as $MoS_{2-x}O_x$ solid solution[18] has been demonstrated. A high resolution XPS spectrum for the sputtered film gave a sulfur doublet with the $2p_{3/2}$ peak at 161.8eV and a smaller $2p_{1/2}$ peak at 162.9eV. This is in good agreement with published results for sputtered films which showed sulfur in the sulfide S^{-2} oxidation state, rather than S^{+4} as in SO_2, S^{+6} as in SO_3, or S^0 as in molecular sulfur.[3] Because of the difference of oxidation state between the sulfur in the film (determined by XPS) and in the vaporizing sulfur species (determined by TDS) the formation and subsequent vaporization of SO_2 indicates that a chemical reaction occurred as a result of heating. Several possible sources of reactive oxygen are adsorbed water, adsorbed oxygen, molybdenum oxides, oxysulfides, and hydroxides.

In Fig.6, the oxidation state of molybdenum was determined before and after heating. In the case of sputtered films only Mo(IV) was seen with no observed change upon heating to 875K. Also shown is the effect of ion-implantation on the oxidation state of molybdenum in the sputtered film. Heating to 875K, a temperature sufficient to desorb all the low temperature SO_2, has little or no effect on the oxidation state of molybdenum. Ion-implantation, however introduces some higher oxidation state as evidenced by the higher binding energies (i.e. >234 eV).

XPS results also showed that oxygen is a major component of the film and this is in agreement with TDS which showed large amounts of SO_2. An absolute comparison of the relative amounts of SO_2 and S_2 cannot be done on the basis of the TDS peak areas without first

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determining the ionization cross sections of the molecules. The atomic composition of a sputtered film as determined by XPS is shown in Table 2 along with RBS results for the same film. These results show that the S/Mo ratio is considerably lower than the 2:1 expected for the stoichiometric compound MoS_2. The (S+O)/Mo ratio however, is close to 2 which is consistent with the $MoS_{2-x}O_x$ solid solution model where oxygen is substituted for sulfur in the film.[18]

Figure 7 shows the 64 amu spectrum for a film of burnished MoS_2 crystals taken with the same instrument and settings used for the sputtered film shown in Fig.5. Under these identical conditions a valid comparison between samples can be made. It can be seen that the relative amount of SO_2 from the sputtered film is much greater than from the burnished MoS_2 film. In the case of the burnished film, the high temperature peak at 1413K gave an area ratio of $[(M+2)/M]=8.94 \times 10^{-2}$ indicating essentially pure S_2 (absence of SO_2) desorption. The extent of burnishing was just sufficient to get the MoS_2 crystals to stick to the foil resulting in a dull grey film. In previous TDS studies[19,20] MoS_2 crystals were vigorously rubbed till a shinny film on the foil resulted. Those results showed an increased amount of SO_2 when compared with the present results. There is some indication that the amount of SO_2 desorption at lower temperatures (<1000K) can be influenced by the burnishing. However, since the burnishing was not done under controlled conditions no definite conclusions can be drawn at this time.

Figure 8 shows the overlay of the 18 amu and the 64 amu desorption spectra for H_2O and SO_2 respectively. Water desorption appears to accompany the SO_2, as indicated by the presence of two low temperature desorption states near 486K and 627K. A desorption state near 752K is not apparent in the 18 amu spectrum. Figure 9 shows a similiar relationship between H_2O and SO_2 for a burnished MoS_2 films. In this case both the SO_2 and H_2O peaks have maxima near

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652K.

Figure 10 shows the high resolution spectra of the Mo(3d) doublet for a heavily burnished (shinny) MoS_2 film before and after heating to 720K. The raw data are shown as dots and the results of peak syntheses using a Lorentzian fit based on MoS_2, MoO_2, and MoO_3 are shown as lines. For the unheated sample the peak at 228.9 eV is interpreted as the Mo(IV) $3d_{5/2}$, the 232.1 eV peak as the sum of Mo(IV) $3d_{3/2}$ and Mo(VI) $3d_{5/2}$, and the 235 eV peak as the Mo(VI) $3d_{3/2}$ signal. The heating to 720K which should have desorbed SO_2 and H_2O from the 652K state, produced a dramatic effect in the Mo(3d) spectrum. Most notable is the disappearance of the 235 eV signal which shows the loss of Mo(VI). Peak synthesis was made using 24, 43, and 33 percent for MoS_2, MoO_2, and MoO_3, respectively, for the unheated sample. For the heated sample, percentages of 17 and 83 percent for MoS_2 and MoO_2, respectively were used. The numerical results of the syntheses are only qualitative but do show a highly oxidized surface and the presence of Mo(VI) before heating. An earlier XPS study of burnished films also showed the formation of Mo(VI) under sliding conditions,[11] and a more recent study of sputtered films exposed to humidity indicated complete oxidation to Mo(VI).[3]

Figure 11(a) is an electron micrograph of a sputtered film and shows that the film is composed of small loosely packed crystals. With an electron beam incident 70° from the surface normal at a magnification of x10,000, the thickness was determined to be 1.6 microns. The film appears to have grown as platelets perpendicular to the substrate. Figure 11(b) is an electron micrograph of the film heated to 1500K, where the high temperature state was completely desorbed. Auger spectra of an unheated sample and one heated to 1100K gave sulfur, molybdenum, carbon, and oxygen signals but no tantalum substrate signal. When heated to

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1500K a strong tantalum substrate signal resulted. This showed that the dramatic change in film morphology seen in Fig.11(b) begins above 1100K and appears to occur along with the high temperature desorption state shown in Fig.5. The WDS analysis showed a 96 percent decrease in the sulfur signal and a 10 percent decrease in molybdenum signal on heating to 1500K. Since no molybdenum species were seen vaporizing from the film with TDS the loss of molybdenum signal must result from the loss of excitation efficiency due to the dramatic change of the film structure.

Previous reports have shown that ion-implantation can have a beneficial effect on the lubricating properties of MoS_x films.[28-30] To determine if TDS could be useful to characterize some effects of implantation, MoS_x and burnished MoS_2 films were implanted with 60keV and 86keV N^+ ion at doses of 2 and $3x10^{17}$ions/cm^2 respectively. The desorption spectra of a sputtered film and an ion-implanted sputtered film taken using the XPS-TDS system are shown in Figures 12(a) and (b), respectively. The ion-implantation modified the film, reducing the amount of SO_2 desorbing below 1100K by about a factor of six. A similiar reduction was also seen with ion-implanted burnished films of both MoS_2 and WS_2.[19,20] Since the samples were heat sinked during implantation, the film material should not have reached temperatures sufficient to desorb the SO_2. From the spectra, a decrease in SO_2 can be seen, in particular the highest desorption state near 750K was preferentially depleted. This depletion is not indicative of a simple heating effect since that would favor desorption of the lowest temperature states. Figure 11(c) shows that the film surface morphology was dramatically altered by the impinging ion beam.

DISCUSSION

Thermogravimetric analysis (TGA) which measures weight loss during heating, has been employed in the past to study the decomposition of bulk MoS_2 and WS_2 solids. Some other TGA experiments have studied the effects of oxygen,[31] dry air, and moisture.[32] These TGA studies provided a means of determining the onset of decomposition for the bulk solid. Typically thermal methods such as TGA and differential thermal analysis (DTA) are used to study samples of bulk material rather than thin films. Thin film DTA experiments[33-35] have been reported for films with masses in the range of hundredths of a milligram. Only one film TGA experiment,[36] however, was found in the literature and this studied the decomposition of diamond films which weighed about one milligram. In principal TDS is related to TGA, since weight is lost through vaporization during heating. In the present experiments, TDS provided more information than TGA by identifying the chemical species and the temperatures involved in decomposition processes taking place directly in thin films on the order of tenths and hundredths of a milligram. The TDS results presented here have shown that the technique can be easily applied to thin films on the order of a few hundredths of a milligram or more.

A TGA study in oxygen where the temperature was raised linearly, showed that fine MoS_2 powder gave a maximum rate of weight loss between 628 to 648K.[31] These TGA results are similiar to the TDS results for the burnished film which gave the maximum rate of SO_2 vaporization at 652K shown in Fig.9. The close comparison is remarkable considering the large difference in ramp rates used: 0.05-0.1 K/sec for the TGA and 7.5 K/sec for the TDS. The sputtered film results are more complex but do have a peak at 627K corresponding to the TGA results. One TDS study of MoS_2 was found in the literature and examined the adsorption sites

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for CO, CO_2, and O_2 on powder and exfoliated (single layer) forms.[37] The TDS temperature range for that study was between 300K and about 470K and no mention was made of SO_2 desorption.

In one early study, a mass spectrometer was used during the TGA experiment to monitor the sulfur vapors produced as a pressed compact of MoS_2 was heated.[10] The onset temperature for weight loss was 1200K. A practical onset temperature for the 1402K peak in Fig.5, and the 1413K peak in Fig.6, can be chosen somewhat arbitrarily to be about 1150K. The TDS is an extremely sensitive measure of the onset, so in Fig.6(b) it can be seen that the experimental onset temperature does not correspond to a fixed temperature but is dependent on the sensitivity of the instrument. The TDS results are in good agreement with the 1200K onset of weight loss reported in the TGA study. This agreement is surprising when considering that the TDS involved thin films containing greater than four orders of magnitude less material than used in the TGA experiment. In the TGA experiment, the mass spectrometer first detected sulfur at 1366K. The mass spectrometer detection was less sensitive than weight loss because of the relatively long distance to the sample and the lack of a line of sight path. With TDS, the thin film was placed in a line of sight arrangement and in close proximity to the entrance aperture of the mass spectrometer ionizer. Table 3 shows a comparison between TDS and both the low and high temperature weight loss experiments.

Early adsorption isotherm studies showed that the amount of water vapor adsorbing on powdered molybdenum disulfide was proportional to the extent of surface oxide. Also an oxide-free surface was found to be hydrophobic.[38,39] A later study showed that weight gain due to water adsorption on MoS_2 powder was lost only when heated in vacuum up to temperatures between

623K and 643K.[40] The water TDS spectra in Figures 8 and 9, have their largest peak at about 650K which is not far from the temperature range found in water adsorption studies.

In separate studies, adsorption of oxygen and other gases were found to take place on the edge plane of MoS_2 crystals, while the basal plane was practically inert. These studies showed that the ability of MoS_2 to catalyze chemical reactions correlates with the edge plane surface area but not the basal plane area.[41] Since sputtered MoS_x crystals and MoS_2 have a similiar structure and adsorption behavior, then based on the small size of the crystals it can be expected that considerable amounts of oxygen are adsorbed. Furthermore, from the water isotherm studies it can be inferred that an amount of water proportional to the surface oxide is adsorbed on the sputtered crystals.

The XPS results reported here showed that molybdenum and not sulfur was oxidized, suggesting that oxygen is attached to molybdenum, probably in the form of some molybdenum oxide, hydroxide, or oxysulfide. Molybdenum was in the Mo(IV) state in the sputtered film and both the Mo(IV) and Mo(VI) states in a burnished film. For the formation and subsequent vaporization of SO_2, a chemical reaction must have occurred which oxidized sulfur in the film during heating. This chemical reaction does not appear to be limited to the crystallite edge plane area, as evidenced by the large amount of SO_2 desorption product.

Some amount of oxygen and water are present in the sputtering system and could be incorporated into the film during growth. Furthermore, some SO_2 must result from oxygen species in the bulk and not from simple adsorption on the surface. Exposure to air after removal from the sputtering chamber can result in the incorporation of oxygen as adsorbed species (e.g. H_2O and O_2) or with long exposure the formation of an oxide. One reasonable explanation for

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the SO_2 desorption states at 627K for the sputtered film and at 652K for the burnished film is desorption from the edges and possibly grain boundaries. Larger particles will have a smaller surface area to volume ratio and the MoS_2 crystals used for the burnished films were as large as 10 microns whereas the MoS_x crystals (Fig.11(a)) were much smaller. This explains the relatively small amount of lower temperature SO_2 observed for the burnished compared with the sputtered films.

The sputtered film SO_2 peak at 752K and the argon peak at 730K occur in a narrow temperature range. This kind of behavior is not typical of a simple chemical decomposition process (i.e. first or second order reaction) and may instead be the result of a structural transformation which releases trapped argon and some oxygen carrier that results in the SO_2 desorption product. In the ion-implanted samples the amount of SO_2 and water were reduced. One explanation for this effect is that the ion-beam modified the lubricant film reducing active sites for SO_2 production. A recent study showed that implantation can reduce film thickness and increase the film density.[30] Increasing the density may reduce the surface area and decrease adsorption of water and oxygen. The high energy ions may also stimulate desorption of adsorbed oxygen species, modify reactive oxide species, or modify active sites involved in SO_2 production.

A final point of interest is the origin of argon in the film. The trapping of argon in sputter deposited films is known to depend on bias voltage and sputtering pressure,[42] so it is not surprising to find it in MoS_x films. The MoS_2 layer lattice structure has a large separation (6.15 nm) between layers[43] so argon can, at least in part, be trapped between the layers within the crystals. A recent study of the structure of sputtered crystallites using transmission electron diffraction showed that the distance between planes in sputtered crystals is between 12 and 15

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percent greater than found with natural MoS_2 from molybdenite.[43] The incorporation of argon in the film structure may have a direct relationship to this increased distance.

CONCLUSION

The TDS results presented showed that both sputtered MoS_x and burnished MoS_2 films decomposed primarily through vaporization of SO_2 and S_2. With this technique the onset temperature and temperature ranges for various decomposition processes were determined. Significant sulfur dioxide vaporization begins as low as 425K for a sputtered film and 450K for a burnished film. Desorption spectra showed two distinct SO_2 peaks at 627K and 752K for the sputtered film and a peak at 652K for the burnished film. XPS results at room temperature showed sulfur in the S^{-2} oxidation state which suggests that, as the temperature increases, a chemical reaction takes place within the film, oxidizing the sulfide which vaporizes as SO_2. The relative amount of SO_2 produced from film decomposition is dependent on the film preparation technique and treatment. This dependence is complex, and may be related to the active surface area of the film. TDS showed that below 1100K, a roughly proportional amount of water vaporizes along with SO_2. The detailed mechanism of sulfur oxidation and the importance of water, however, remain to be determined.

At higher temperatures, sulfur dissociates from burnished and sputtered films. In the absence of other degrading effects such as oxidation, a temperature of about 1150K could be set as the high temperature limit of lubricant stability. TDS also revealed that argon was trapped within the film during the sputtering process and was released at various temperatures along with the water and sulfur products.

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Correlations between the TDS results and performance parameters such as friction coefficients and lubricant lifetime should be considered for real tribological systems. The present results clearly showed SO_2 and water desorption at low temperatures. Controlled exposure of solid lubricant films to water, oxygen, and other gases can help to clarify the complex interactions involved. Since the TDS technique showed that decomposition was dependent on the film application technique (eg. sputtered, implanted, and burnished), it should also be sensitive to various other techniques such as ion-plating, co-sputtering etc. Finally, TDS should be considered for studies of the thermal and chemical degradation of a wide range of films of tribological interest such as oxides, nitrides, sulfides and selenides.

ACKNOWLEDGEMENTS

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LIST OF FIGURE NUMBERS AND TITLES

MASS FILTERED IONS

Q.M.S.

SURFACE

ELECTRON BOMBARDMENT
IONIZATION SOURCE

SURFACE POSITIONING
DEVICE

AUGER ELECTRON
SPECTROMETER

Fig. 1- TDS-System; multiple solid lubricant film samples are analyzed with TDS and Auger.

Fig. 2- **High Temperature Thin Film TDS Assembly**; 1)solid lubricant coating, 2)tantalum foil, 3)thermocouple, 4)high temperature steel alloy, 5)copper current wire, 6)sample support housing, 7)alumina spacers, 8)alumina thermocouple support tube, 9)adjustable thermocouple support, 10)machinable glass thermocouple loader, 11)support rod.
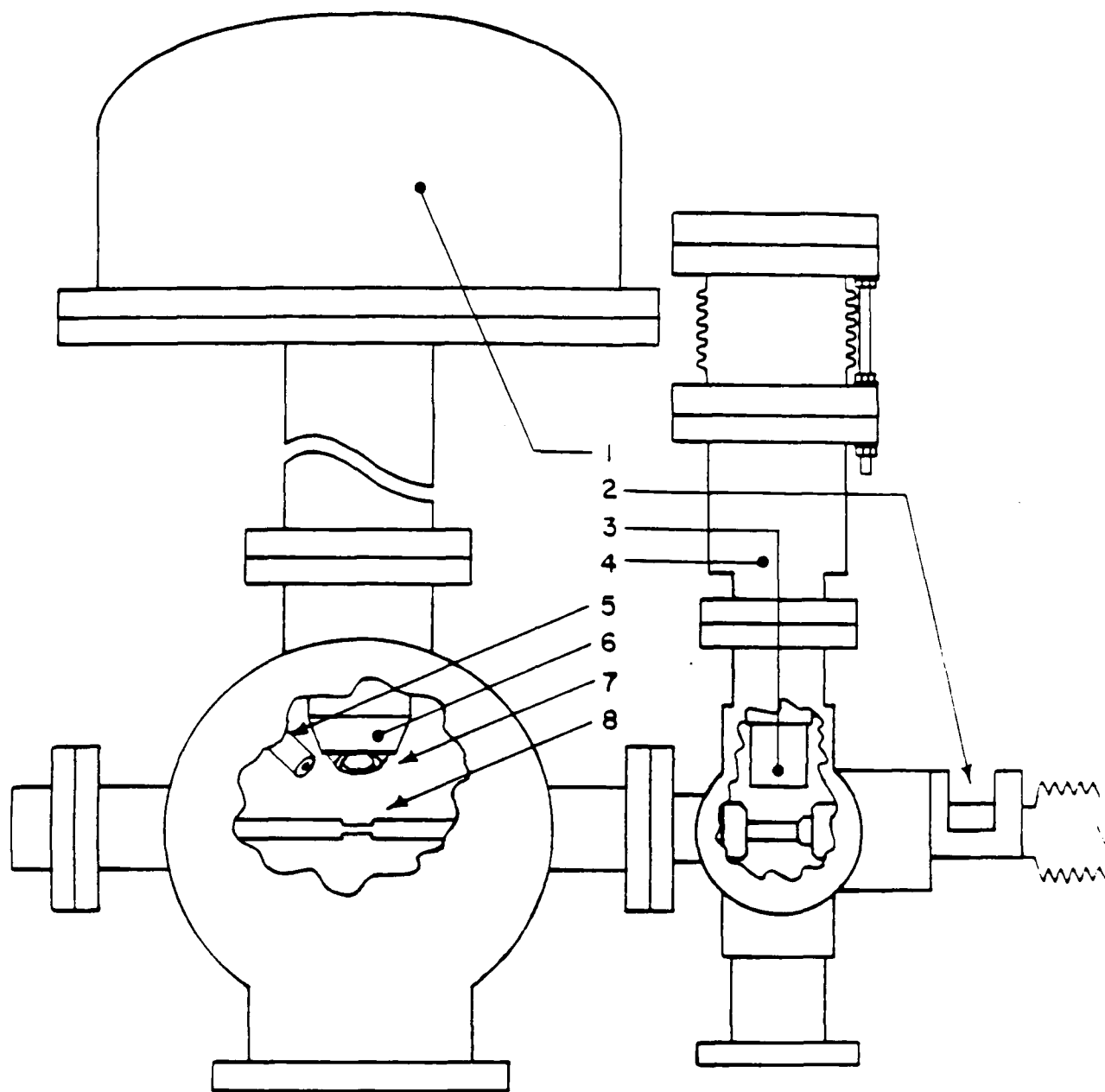
Fig. 3- **The XPS-TDS System;** 1)hemispherical energy analyzer, 2)sample introduction area, 3)mass spectrometer, 4)adjustable mass spec. housing, 5)electron gun for Auger, 6)electron energy analyzer entrance, 7)X-Ray source, 8)sample area of heated probe.
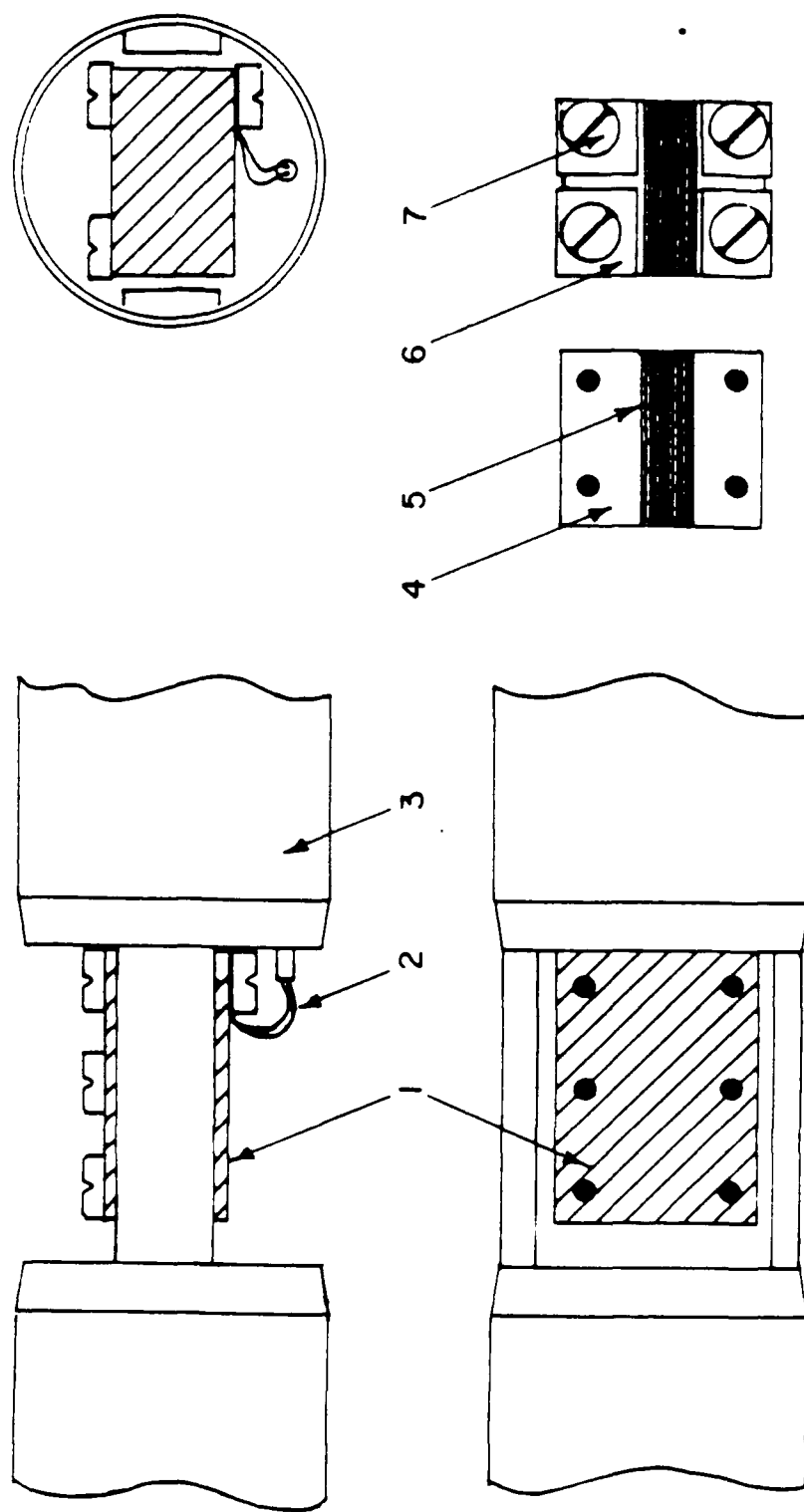
Fig. 4- **XPS-TDS Sample Arrangement;** 1)probe heater block, 2)thermocouple, 3)sample rod, 4)tantalum foil sample, 5)solid lubricant coating, 6)tie-down washers, 7)gold plated screws.

Table 1- Comparison of Relative TDS Peak Areas for Sputtered MoS$_x$ Films

Mass(amu)		64	66	48	50	40	18	80	128	160	192
>1100K	species	S$_2$+SO$_2$		SO		Ar	H$_2$O	S$_2$O	S$_4$	S$_6$	S$_8$
	area	1	0.074	0.38	0.015	0.59	no peak	0.025	≤ 0.003		
<1100K	species	SO$_2$		same as above							
	area	0.40	0.020	0.27	0.012	0.76	0.90	no peaks			
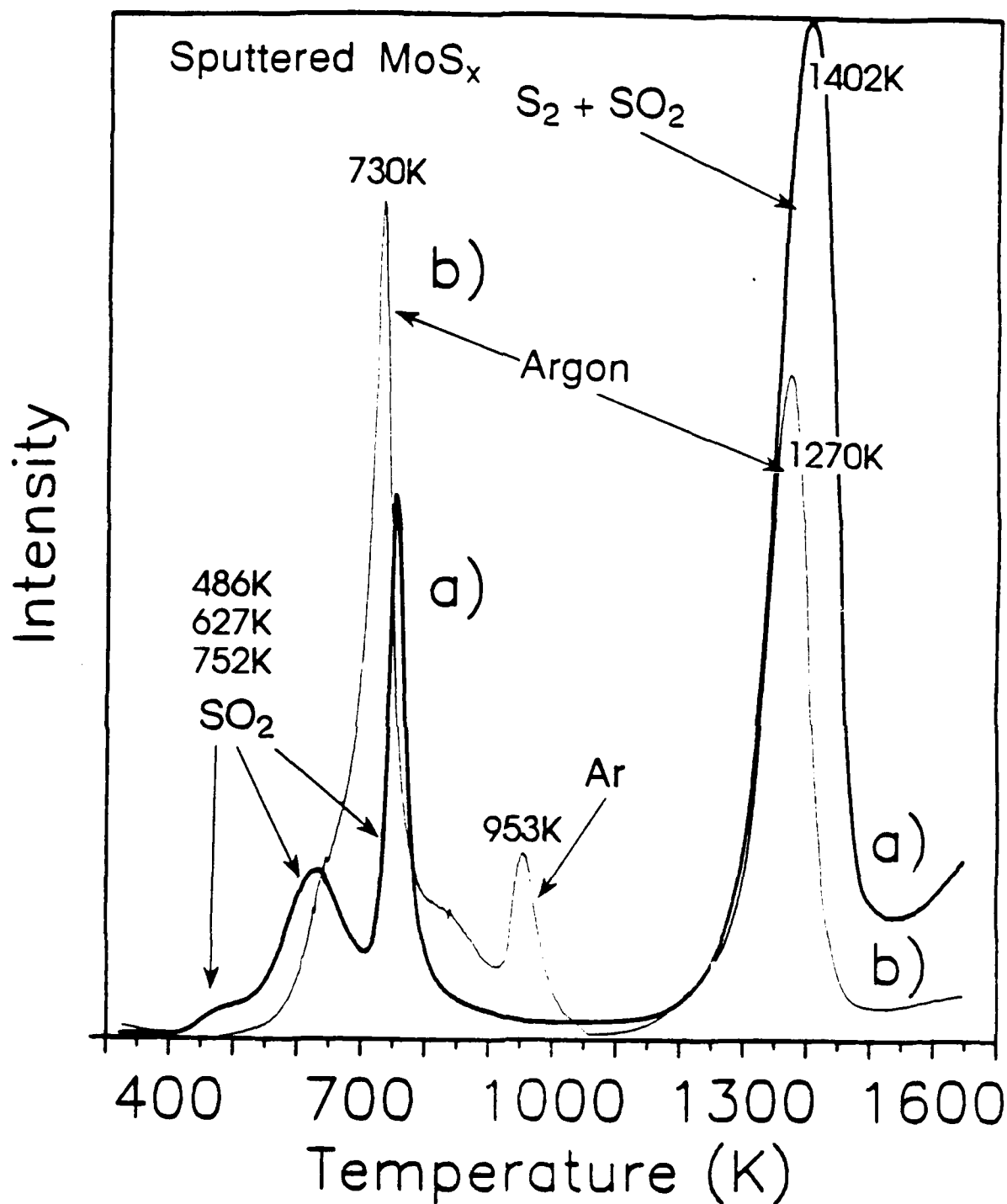
Fig. 5- TDS of sputtered MoS_x film: a) SO_2 below 1000K and $S_2 + SO_2$ above 1000K and b) argon releasing at various temperatures.
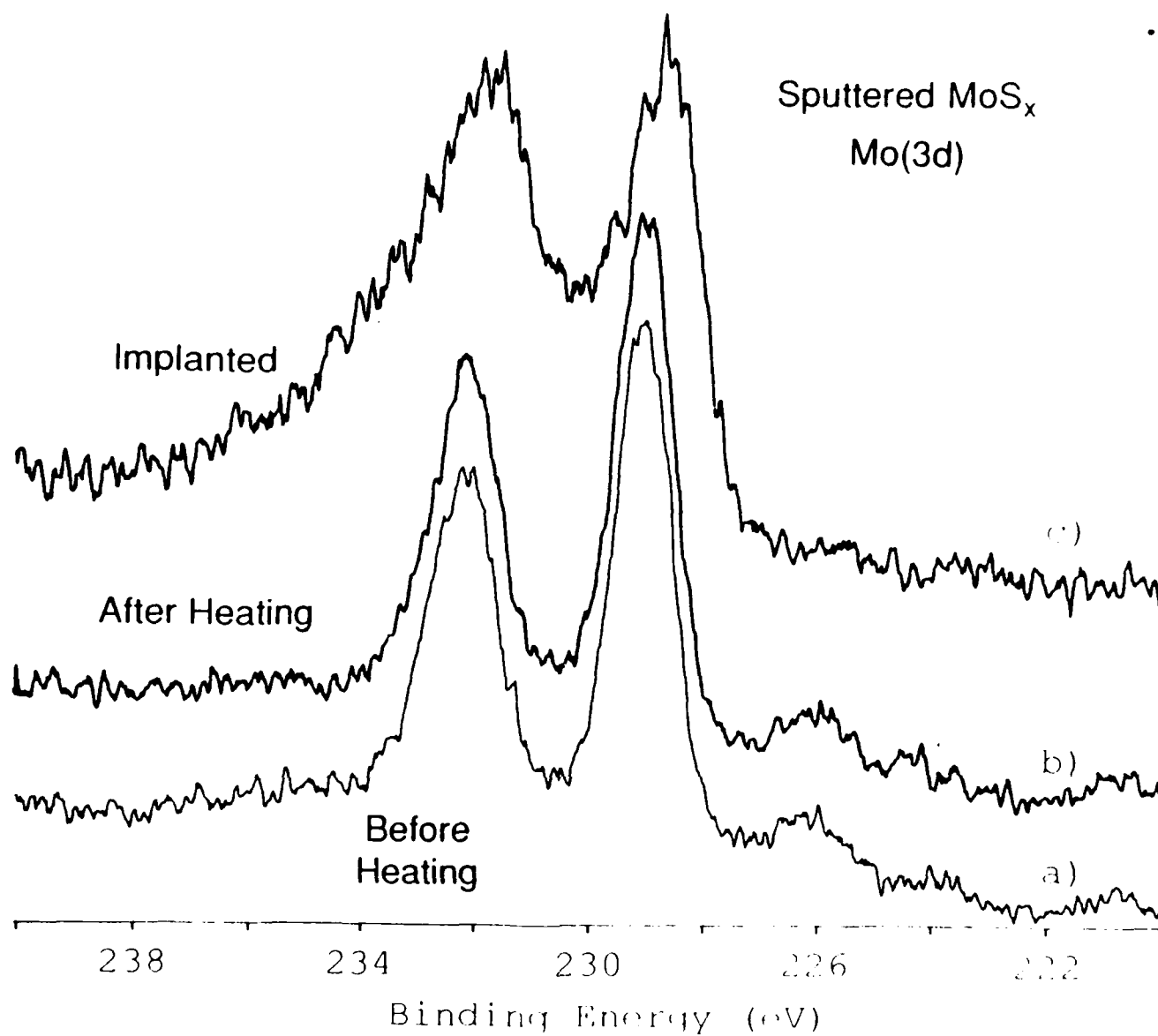
Fig. 6- XPS high resolution Mo(3d) spectra: a)sputtered MoS$_x$ film. b)after heating to 875K. c)after N$^+$ ion-implantation.

Table 2- Atomic Composition of Sputtered Film				
	S/Mo		(S+O)/Mo	
Method	Ambient	~875K	Ambient	~875K
XPS	1.31	1.66	1.94	2.21
RBS	1.44			
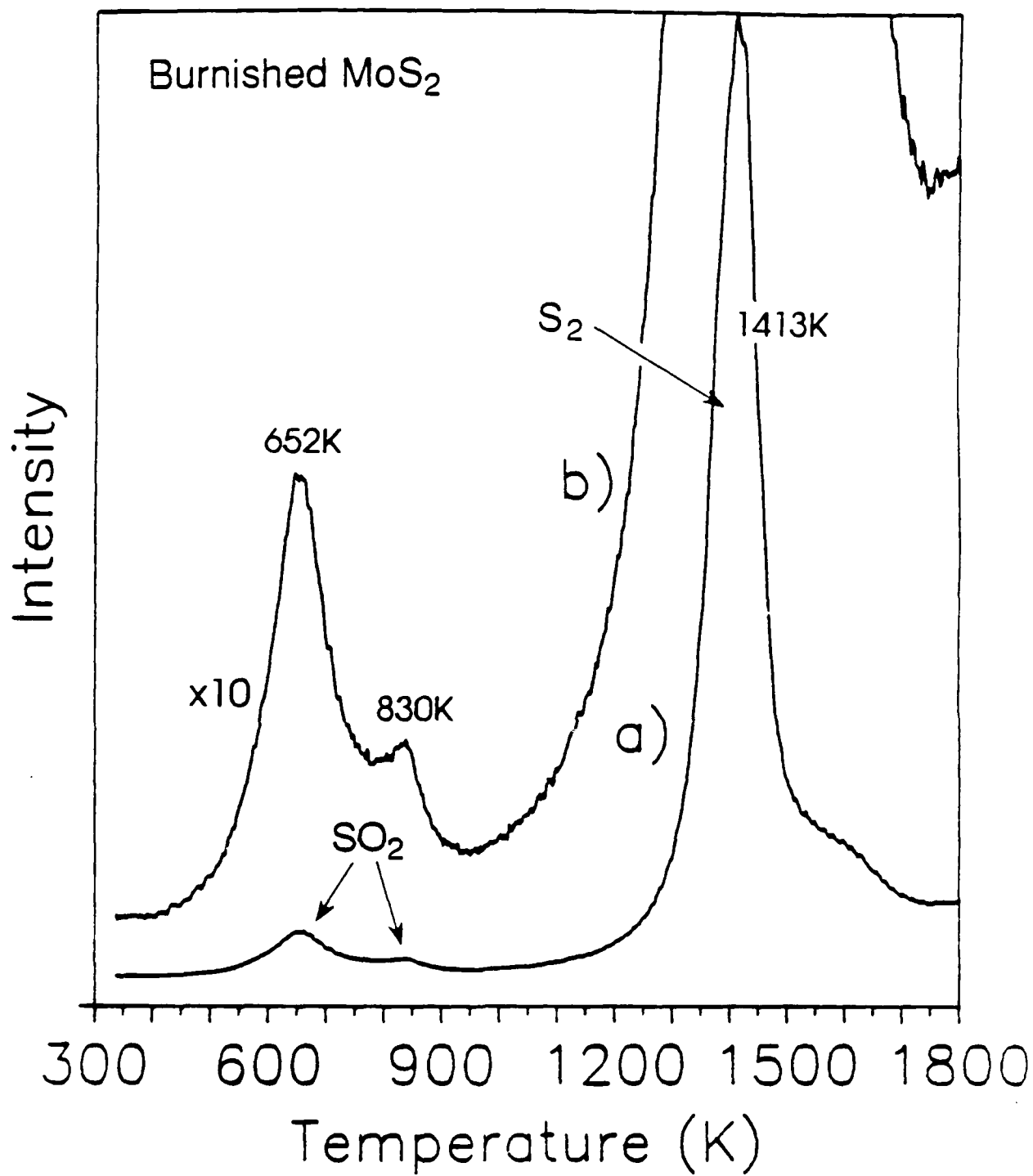
Fig. 7- TDS of film lightly burnished from MoS_2 crystals; a) SO_2 below 950K and S_2 above 950K, b) scale x10.
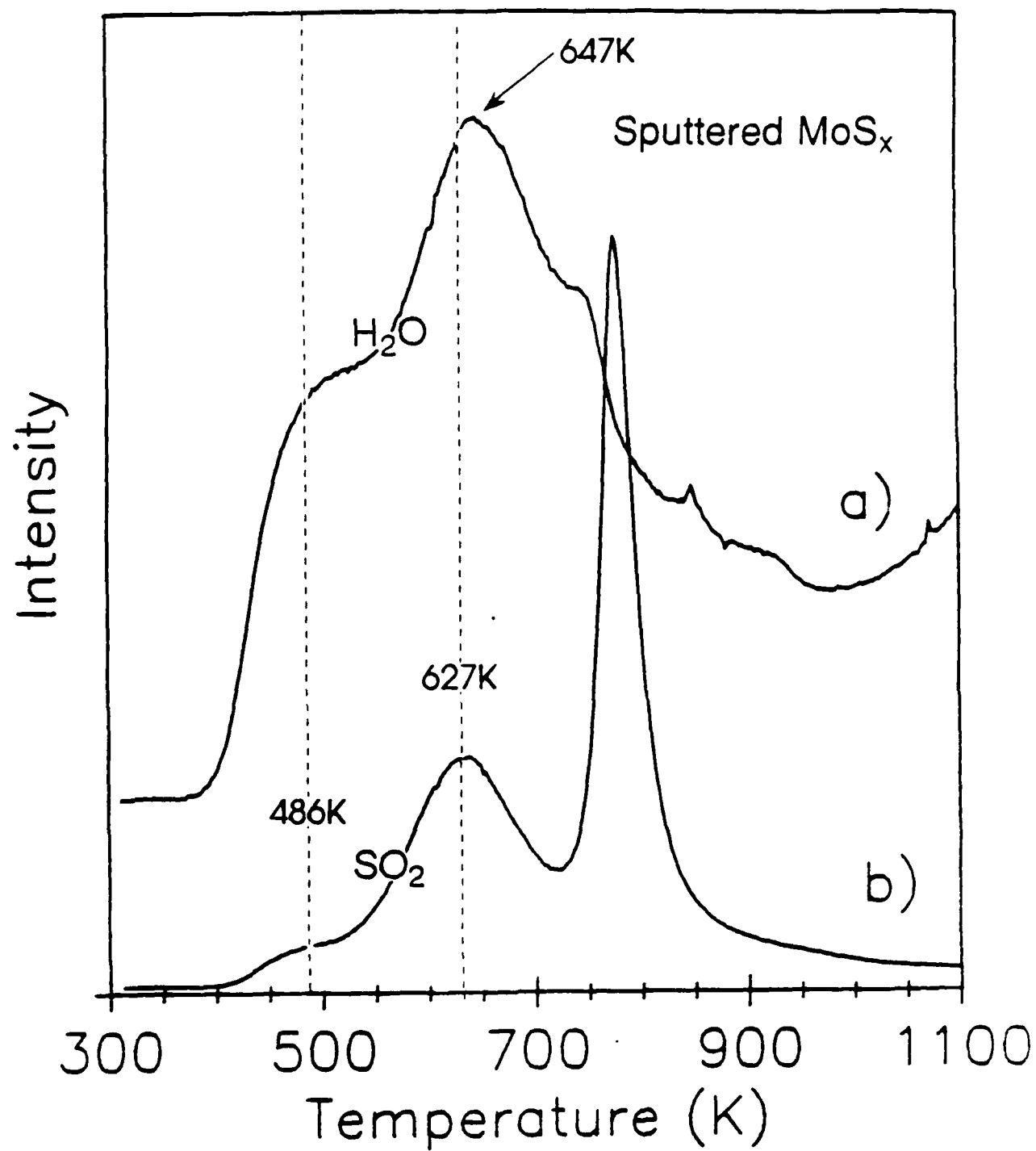
Fig. 8- TDS of sputtered MoS_x film shows a) H_2O and b) SO_2.
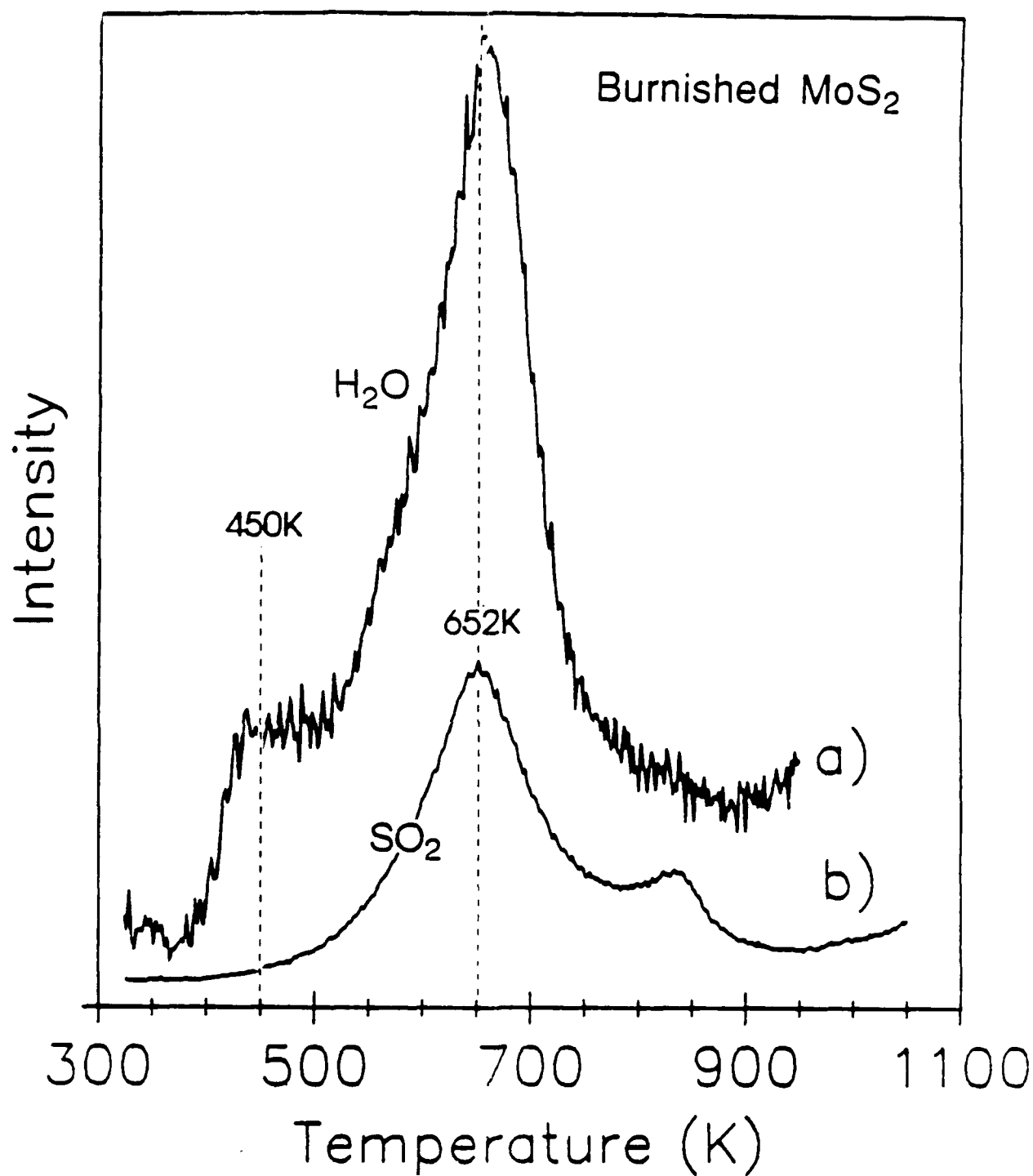
Fig. 9- TDS of film burnished from MoS_2 crystals: a) H_2O and b) SO_2.
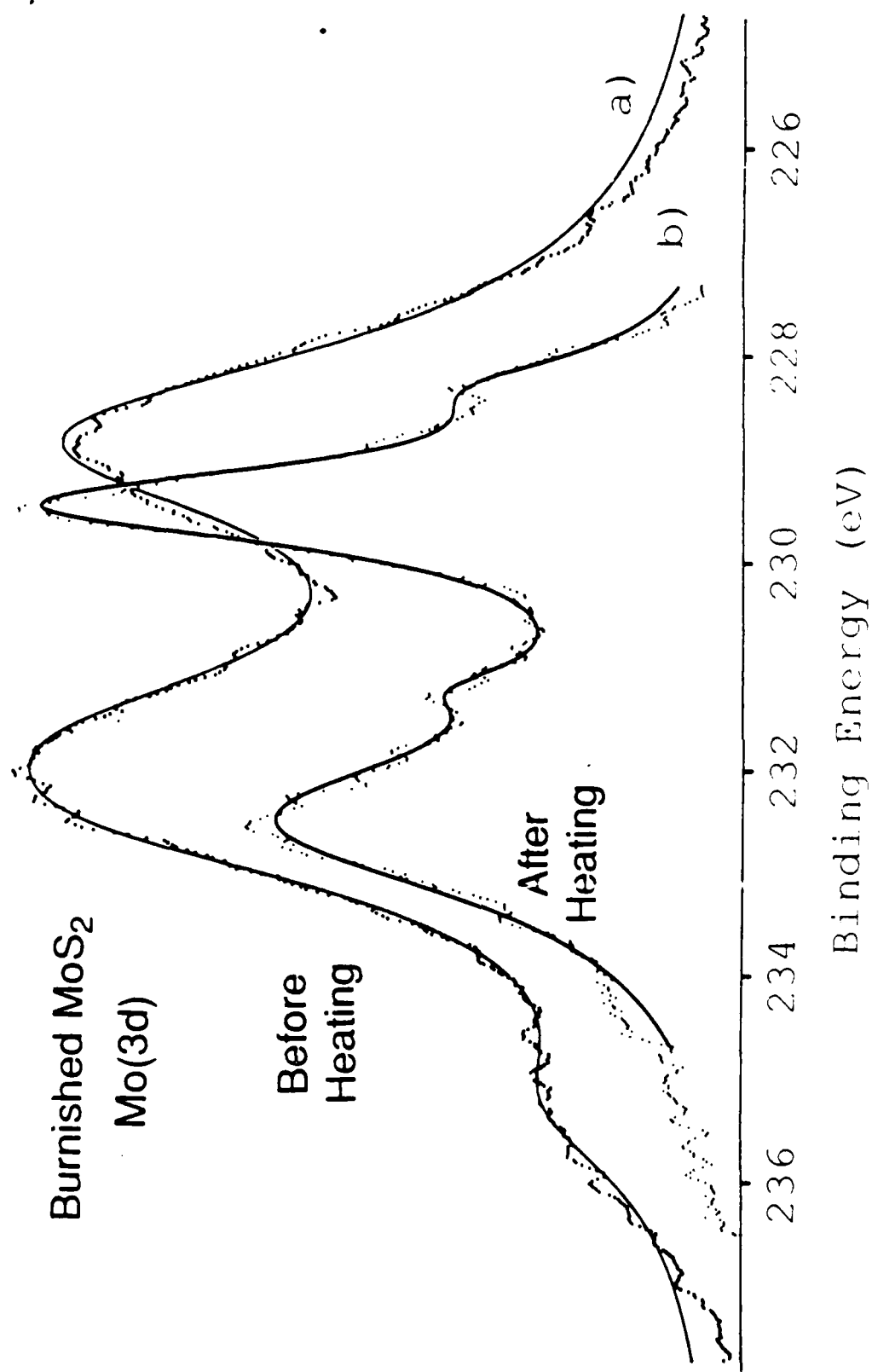
Fig. 10- XPS high resolution Mo(3d) spectra for a highly burnished film with raw data shown along with Lorentzian fits: a) MoS$_2$ film before heating and b) after heating to 720K.
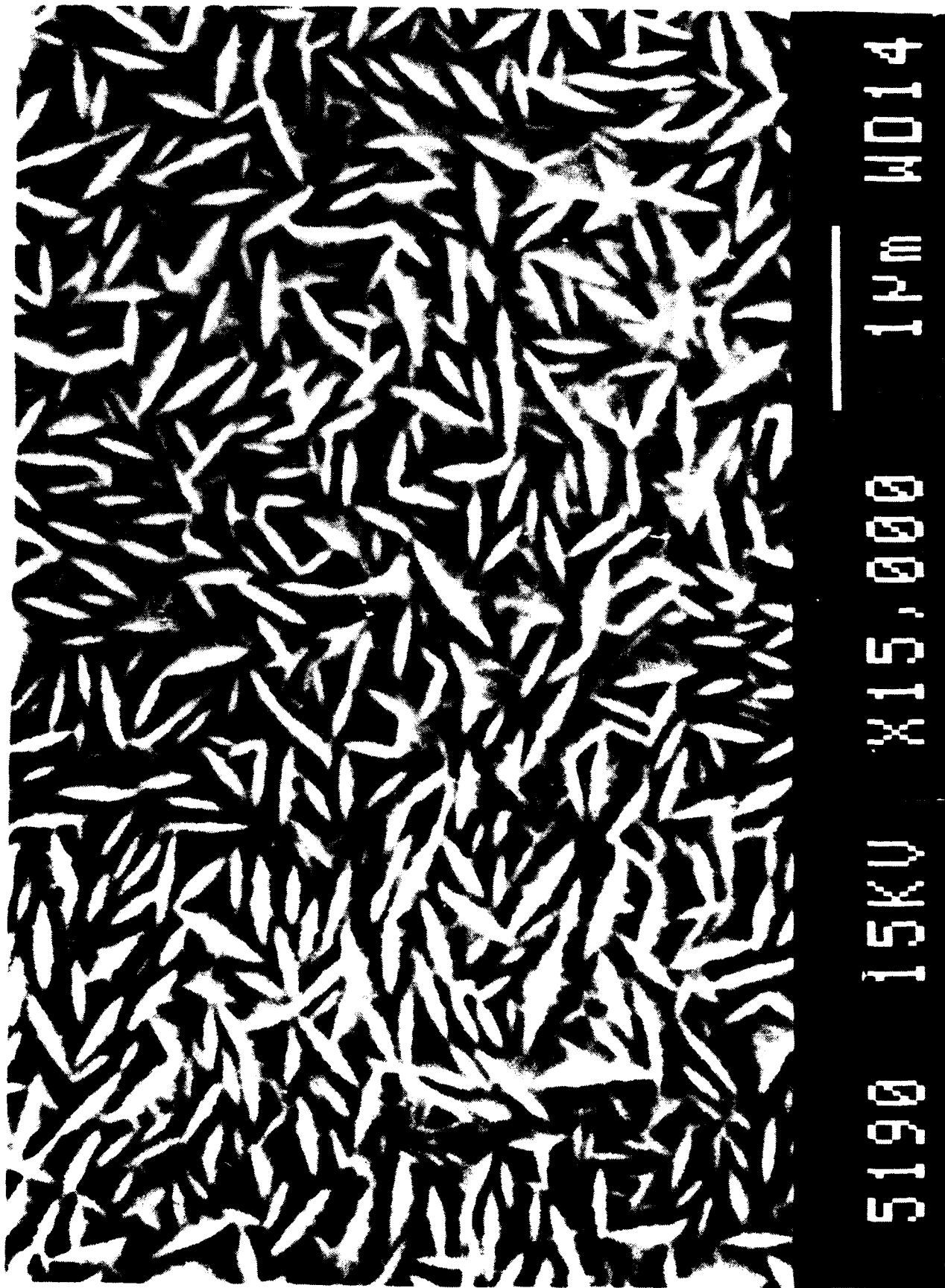
Fig. 11a - Scanning electron micrograph of sputtered MoS$_x$ at normal incidence to the surface before heating.
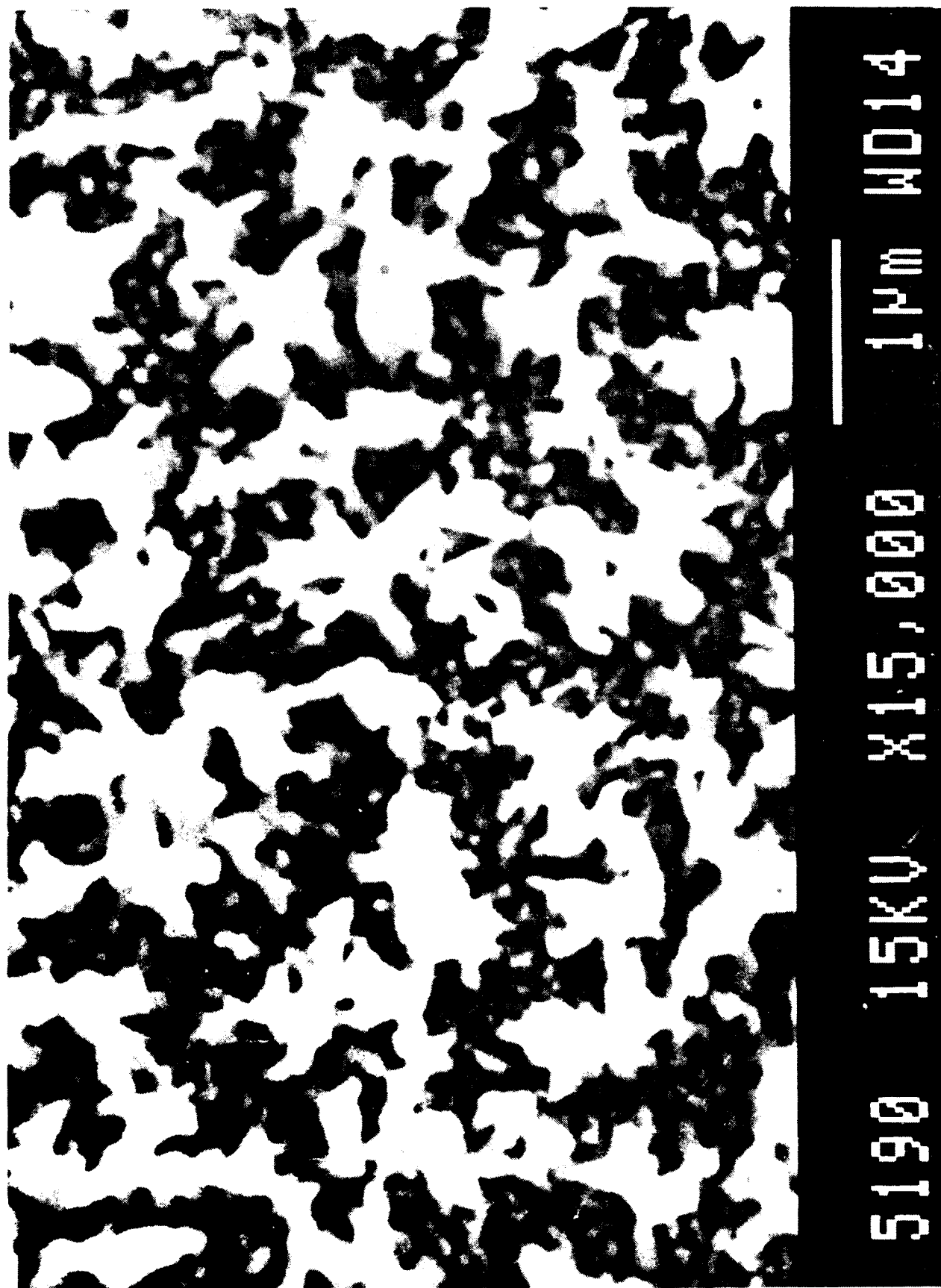
Fig. 11b - Scanning electron micrograph of sputtered MoS_x at normal incidence to the surface after heating to 1500K.
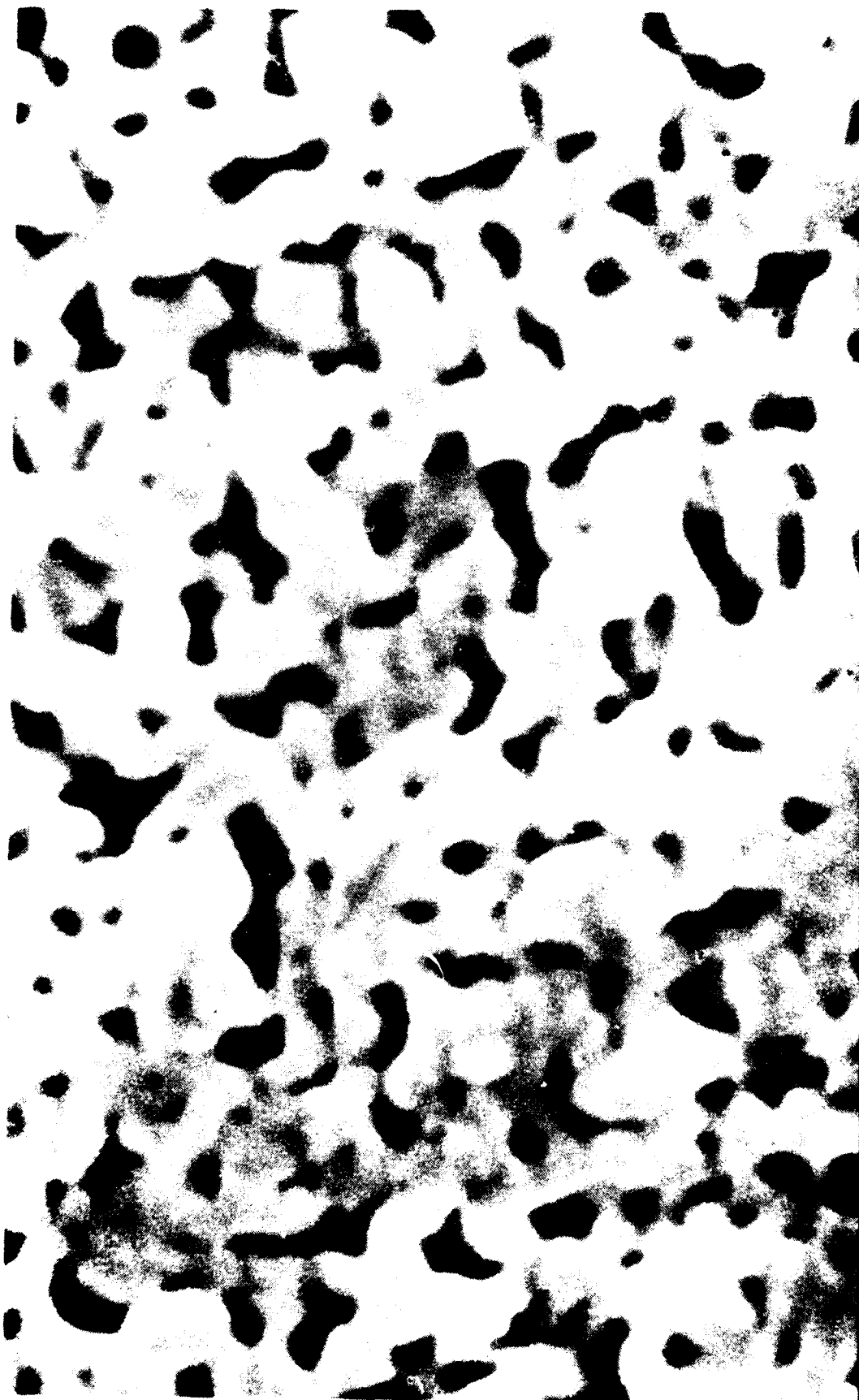
Fig. 11c - Scanning electron micrograph of sputtered MoS$_x$ at normal incidence to the surface after 60 keV N+ implantation.
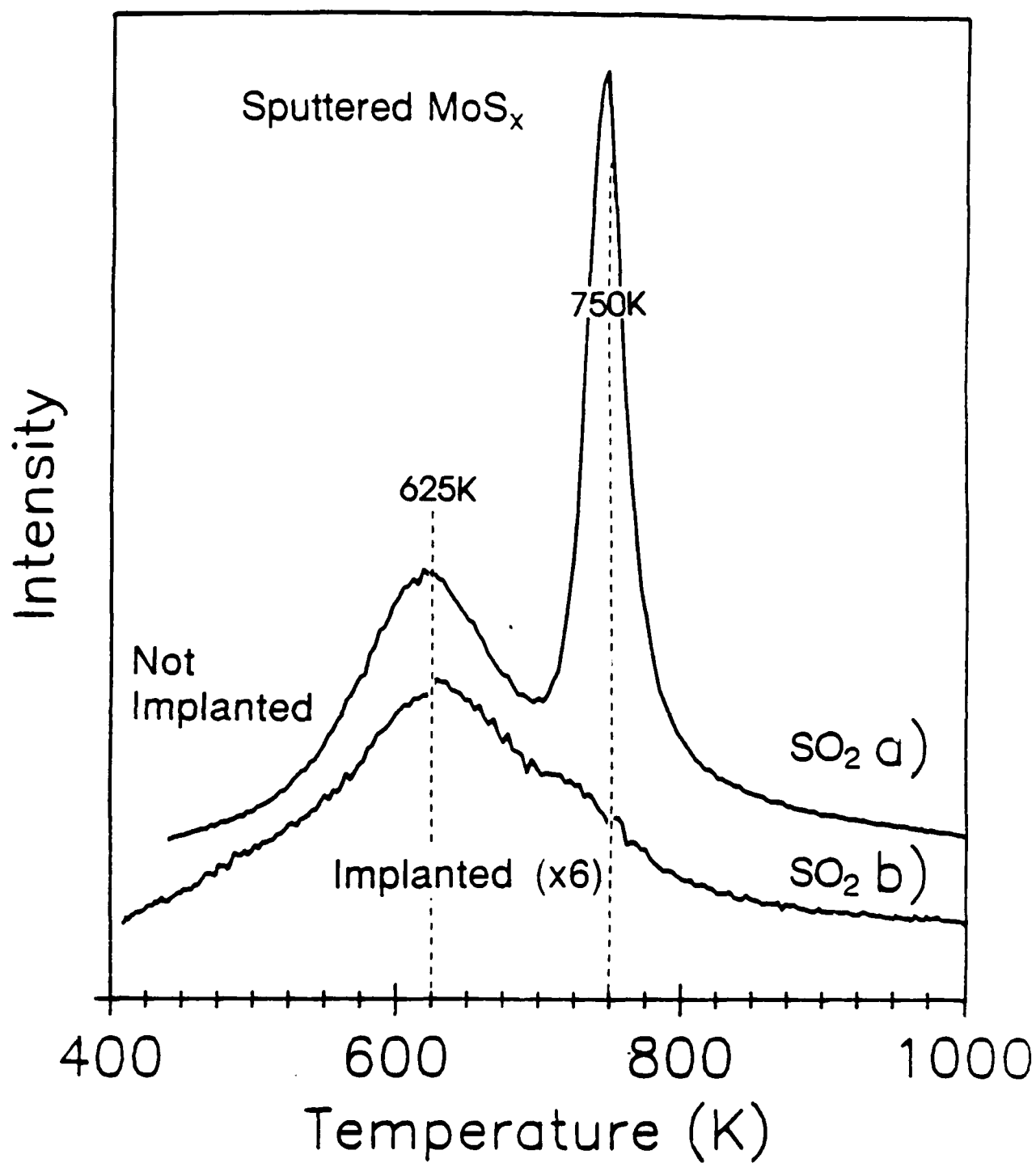
Fig. 12- TDS of sputtered MoS_x film a) before ion-implantation (scale x1) and b) after ion-implantation (scale x6).

Table 3- Comparison of TDS & TGA		
	TDS	TGA
Sample Type	Sputtered (S) and Burnished (B) Films	Powder
Mass of Sample	10 - 300 μg	100-200 mg
Onset of Low Temp. Decomposition	Mass Spec. identified SO_2 and Water beginning at 450 K (S) 410 K (B)	Weight Loss at $\approx$ 520 K (Ref. 31)
Peak Temperature	627, 752, & 486 K (S) 652 K (B)	628 - 648 K (Ref. 31)
Onset of High Temp. Decomposition	S_2, SO_2 etc. identified $\approx$ 1150K	Weight Loss at $\approx$ 1200 K S_2 identified at $\approx$ 1366K (Ref. 10)
Peak Temperature	$\approx$ 1425 K	----

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Key Words

Solid lubricants
Molybdenum disulfide
Mass spectrometry

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EVALUATION OF SOLID LUBRICANTS: THE CHEMISTRY
OF SPUTTERED MoS$_x$ FILMS USING COMBINED THIN
FILM ANALYSIS TECHNIQUES - Daniel E. Pierce,
Richard P. Burns, Helen M. Dauplaise, and
Lawrence J. Mizerka

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Thermal desorption spectroscopy (TDS) is introduced as a diagnostic tool for deter-
mining the thermal stability of solid lubricant films. In particular, TDS revealed
the temperatures at which various decomposition processes occurred as sputtered films
were heated in vacuum. The primary film decomposition products detected were SO2
beginning at about 425K and S2 beginning at about 1150K. A close relationship
between water desorption beginning about 400K and SO2 desorption exists in the tem-
perature range 400K-800K. Besides chemical decomposition products, a significant
amount of argon trapped in the film during the sputtering process is released at
various temperatures. TDS results for sputtered films were compared with results
for burnished films and with thermo-gravimetric (TGA) analysis, water absorption,
and other relevant studies of molybdenum disulfide found in the literature. TDS
also showed the N ion-beam modification of sputtered films resulted in a decrease
in desorption of SO2. Along with TDS, X-ray photoelectron spectroscopy (XPS) was
used to study the effect of heating on the solid lubricant films. In addition,
scanning electron microscopy (SEM), wavelength dispersive spectroscopy (WDS), and
Rutherford backscattering spectroscopy (RBS) were used to characterize the samples.